

Chemical recycling of polyesters

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Abstract: In the presented paper, two basic strategies that can be used in the processes of chemical recycling of polyester material were described. The first of them involves increasing the molar mass of recycled materials in the solid-state polycondensation (SSP) process and/or joining their chains with various types of substances easily reacting with the end groups of polyesters (so-called extending agents). The essence of the second strategy is the degradation of the material under the influence of various protogenic agents (such as water, alcohols, glycols and amines) to obtain low-molecular products or oligomers that can be used as raw materials in the synthesis of many classes of polymers. The methods that are already used in PET [poly(ethylene terephthalate)] recycling and the possibility of their extension to other types of polyesters are both shown.

Keywords: recycling, solid-state polycondensation, polylactide, poly(ethylene terephthalate), glycolysis, hydrolysis, aminolysis, ammonolysis.

Recykling chemiczny poliestrów

Streszczenie: W pracy przedstawiono dwie podstawowe strategie możliwe do wykorzystania w procesach chemicznego recyklingu tworzyw poliestrowych. Pierwsza z nich polega na zwiększeniu masy molowej utylizowanych tworzyw polimerowych w procesie polikondensacji w ciele stałym (SSP) i/lub łączeniu ich łańcuchów za pomocą różnego typu substancji łatwo reagujących z grupami końcowymi poliestrów (tzw. czynników przedłużających). Istotą drugiej strategii jest degradacja tworzywa pod wpływem różnych czynników protogennych (takich jak: woda, alkohole, glikole i aminy) w celu uzyskania produktów małowcząsteczkowych lub oligomerów, które można wykorzystać jako surowce w syntezie wielu klas materiałów polimerowych. Omówiono metody stosowane już w recyklingu PET [poli(tereftalanu etylenu)], a także możliwość ich rozszerzenia na inne gatunki poliestrów.

Słowa kluczowe: recykling, polikondensacja w ciele stałym, polilaktyd, poli(tereftalan etylenu), glikoliza, hydroliza, aminoliza, amonoliza.

Chemical recycling, also known as feedstock recycling, covers a wide range of processes where post-consumer plastic waste is converted into valuable chemicals. In case of plastic waste being a mixture of different polymers, thermal processes are used to obtain synthesis gas and synthetic oils that can be added to fuels or cracked [1]. However, if it contains only one type of polymer, there is the possibility of more rational use of such material. For example one can improve its mechanical properties as a result of the processes leading to an increase in the molar mass of polymer. The other possibility is decomposition of plastic waste into monomers or intermediates from which various types of valuable polymer materials can be obtained. In our review we will describe these two different strategies, called constructive and destructive recycling, respectively. The discussion will be based on the recycling of poly(ethylene terephthalate)

(PET), whose recyclates are commercially available, and polylactides (PLAs), which are relatively new on the polymer market. They belong to the group of so-called green plastics because they are obtained from natural raw materials and are biodegradable. Initially, it was thought that wastes from polylactide (PLA) would be easily biodegradable in the natural environment or in composting plants [2]. Nowadays we know that this idea is irrational and we should consider their transformation into chemicals more valuable than carbon dioxide and water. In the presented paper we show the possibility of using some chemical recycling methods to utilize other types of condensation polymers.

CONSTRUCTIVE METHODS OF CHEMICAL RECYCLING

Two basic methods are used to increase the molar mass of polyester waste. In the first one, recyclates are subjected to SSP, in which the separation of a by-product occurs, similarly to the synthesis of original materials. The

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second method involves the introduction into the polymer of low molecular weight compounds or oligomers having at least two functional groups capable of reacting with the end groups of polyesters, *i.e.* the hydroxyl and/or carboxyl groups. These types of additives are often called chain extenders (ChEx) because they lead to the coupling of at least two polyester chains, which in turn results in an increase in the average particle length or the formation of branched structures. The grafted polymer may constitute a small fraction of the material, however, its excellent mechanical and rheological properties compensate the loss of the required properties observed in the remaining part of the material. This method can be used as an element of material recycling by companies dealing with polymer processing in order to manage the post-production waste or to reduce the adverse effects caused by partial degradation of the material during processing.

Solid-state polycondensation

Solid-state polymerization is a well-known method for obtaining high molar mass condensation polymers [3, 4]. This process involves the reaction of end groups occurring in the amorphous phase of the partially crystalline prepolymer at a temperature between the glass transition temperature and the crystallite melting point. The reaction takes place according to a two-phase model in which the end groups, by-products and oligomers are excluded from the crystalline phase (Fig. 1). By-products and atmospheric oxygen are removed under reduced pressure or an inert gas flow.

Due to the lower reaction temperature and the limited possibility of penetration of by-products and oxygen into the crystalline phase, the probability of degradation of the chains in SSP processes is much lower than during classic bulk polycondensation. A number of problems associated with the stirring of the viscous melt and heat transport are reduced or eliminated. In some systems, between the elastic amorphous and crystalline phases the rigid amorphous phase is formed which crystallizes with time. With the reaction time, the content and melting point of the crystalline phase increase, thus allowing for a gradual rise in the process temperature. The rate of the process and the molar masses of products also depend on the molar mass of prepolymer, its particle size, the type of catalyst system and the method of removing by-products.

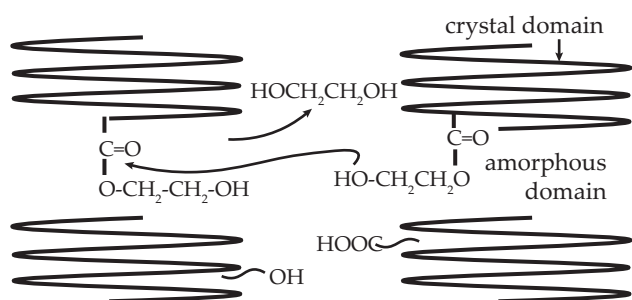


Fig. 1. Solid-state polycondensation

SSP was used to prepare various types of condensation polymers, mainly polyesters such as PET [5], poly(butylene terephthalate) (PBT) [6], poly(propylene terephthalate) (PPT) [7], poly(ethylene furanoate) [8], poly(glycolic acid) (PGA) [9, 10], PLA [10–12], but also polyamides (PA) [13] and polycarbonates (PC) [14]. On an industrial scale, the SSP technique is mainly used for the production and recycling of PET [5, 15–17].

The PET recycling process based on SSP takes from 6 to 20 hours depending on the reaction temperature. In the first stage, the granulate is dried and crystallized at temperature of 170 °C in an inert gas flow. Under these conditions, the content of the crystalline phase reaches approximately 40%, which is necessary to avoid the problem of aggregation of granules during the SSP process. In addition, the rate of the process increases with increasing degree of crystallinity due to the higher concentration of end groups in the amorphous phase. In the next stage, solid-state polycondensation is carried out under reduced pressure at temperature between 220 and 230 °C. During this time, esterification and transesterification processes occur, increasing the molar mass of the polymer. By maintaining adequate purity of the waste PET material, after the SSP process, granules with a molar mass similar to the primary raw material are obtained, and they can be used for the production of packaging for food contact [16, 17].

Installations for the production and recycling of PET by the SSP method already work in many countries. In Poland, they are present in Poznań (MPTS) [18], Bielsko-Biała (Polowat) [19] and Warsaw (Marcato) [20].

As mentioned before, by the SSP method many types of polymers can be obtained, however, their practical use in recycling processes may face significant limitations due to the lack of the sufficient amounts of raw materials, too low values of melting point temperatures of the crystalline phase and the possibility of depolymerization. For example those problems occur during PLA recycling, since the melting point of the PLA crystalline phase is usually in the range of 150–170 °C, and in the amorphous phase the chains can be shortened as a result of the liberation of lactide. Effective performance of such a process requires a very precise temperature regime, selection of appropriate catalysts and conditions for removing by-products [10, 12].

Methods using chain extenders

In scientific research as well as in industrial practice, the most widely used ChEx are additives containing epoxy functions. The chain extension process is based on a nucleophilic substitution reaction with an epoxide ring opening by attack of the polyester end group. Free hydroxyl group and an ether or ester bond are formed, in the case of a reaction with hydroxyl or carboxyl group, respectively. The reactions with carboxyl groups proceed faster than those with hydroxyl groups. Among the

compounds with a well-defined molecular structure having two reactive groups one can list 1,2,7,8-diepoxyoctane or diglycidyl ether of bisphenol A, which were used to strengthen PET and improve the properties of unsaturated polyester resins [21]. In the same work epoxidized vegetable oil was also used as ChEx. In turn, Guo and Chan presented the possibility of improving the tensile strength, impact strength and thermal stability of PBT by reactive extrusion with addition of tetrahydrophthalic acid diglycidyl ether [22]. Similar results were obtained for PET and PBT by using more sophisticated diglycidyl esters of acid containing in its structure fragments of pyromellitic acid diimide [23, 24]. However, styrene-acrylic oligomers having epoxy moieties in their structure are more often used. An example are products manufactured by BASF: Joncryl ADR 4368-C [25] or Joncryl-4300 [26] differing primarily in the number of epoxy groups per molecule and the weight average molar mass. According to the manufacturer's recommendations they can be used to extend PET, PBT, PLA, PA, PC, glycol-modified poly(ethylene terephthalate) (PETG), thermoplastic polyurethane (TPU) or polyoxymethylene (POM) chains. A large number of examples of polyester reinforced with this type of ChEx can be found in the literature. Corre *et al.* used CESA extender containing Joncryl 4368 to modify PLA, which was subsequently foamed with supercritical CO₂. The obtained rheological benefits proved to be vital for expanding the processing window in terms of foaming temperatures. It was found that in supercritical CO₂ the process of crystallization of the extended PLA chains dramatically differs from that of pure PLA chains [27]. The multi-epoxide oligomer was also used by other authors to strengthen pure PLA [28, 29], PLA blend with thermoplastic starch [30], PLA blend with poly(butylene succinate-*co*-adipate) and their composites with nanoclay [31] as well as PLA nanocomposites foamed with CO₂ [32]. Other researchers have shown that multi-epoxy ChEx can be successfully used as reactive compatibilizers of blends of two immiscible polyesters: PLA and poly(butylene adipate-*co*-terephthalate) (PBAT). The interphase formed as a result of the reaction of both polyesters with one ChEx molecule affects rheological properties and improves the tensile strength and elongation at break of the blend [33]. Another strategy for achieving a similar effect deals with the synthesis of a triblock copolymer having a PBAT or poly(butylene adipate) chain as a middle segment and acrylic side blocks rich in epoxy moieties. The reactive processing of such a copolymer with PLA leads to a more flexible material without compromising its strength [34]. In the case of other biodegradable polyester, poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV), the addition of Joncryl ADR 4368 during extrusion increases its thermal resistance, melt viscosity and reduces its crystallization ability, however, the authors do not mention how the modification affects the ability to enzymatic degradation [35]. A large number of papers relate to the modification and strengthening of virgin and

recycled PET or PBT by incorporation of multifunctional epoxy ChEx [36–39], with most of them currently found in Asian literature (mainly Chinese). However, these publications are only available in the native language. Due to the practical aspects these solutions are also the subject of a large number of world patents [40, 41]. An interesting proposition is also the use of epoxy-functionalized polyhedral oligomeric silsesquioxane as a reactive filler for PBT, which also plays the role of ChEx [42].

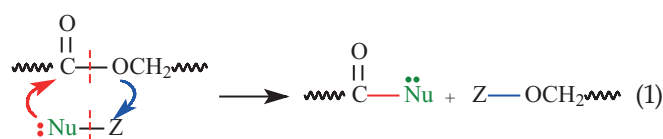
In addition to ChEx based on epoxy groups, one can distinguish some other groups of chemical compounds capable of reacting with the end groups of polyesters. These include diisocyanates (for PET, PBT) [43, 44], tetracarboxylic acid dianhydrides (*e.g.* pyromellitic dianhydride for recycled PET) [45], or combined systems, *e.g.* pyromellitic dianhydride with triglycidyl isocyanurate [46]. The hybrid solution may be the use of 3-isocyanatopropyltriethoxysilane and/or 3-glycidoxypropyltrimethoxysilane in the reaction with PET end groups, resulting in the formation of moisture-curable systems containing siloxane cross-links [47].

For the modification of PET and PBT, quite exotic and rather unsuitable in industrial conditions compounds are also used, *e.g.* bis-*N*-acyllactams [48], cyclic imino-ethers [49], cyclic imino-esters [50]. On the other hand, bis(2-thiazolines) do not show any effect under the test conditions, while one can observe polymer degradation for bis(2-imidazolines), as well as gelation for bis(*N*-acylaziridines) and bis(iminocarbonates) [51].

Almost all of the presented modifications lead to an increase in the average molar mass and melt viscosity of the polymer, partial branching or even crosslinking, and the improvement of mechanical properties, *e.g.* tensile strength and impact strength. For this reason, the use of various types of commercially available ChEx can be safely considered an effective method of constructive chemical recycling of polyesters. The properties of granules obtained in the presence of ChEx can be further improved using the SSP technology [52, 53].

DESTRUCTIVE METHODS OF CHEMICAL RECYCLING OF POLYESTERS

Raw material recycling (destructive recycling, depolymerization) of polyesters usually uses the cleavage of ester bonds present in the chains of these polymers by the attack of selected nucleophilic agents on carbon atoms in carbonyl groups [Equation (1)].



Generally, as nucleophilic agents, compounds with labile hydrogen atoms are used, such as water, alcohols, diols (glycols), ammonia and primary or secondary ali-

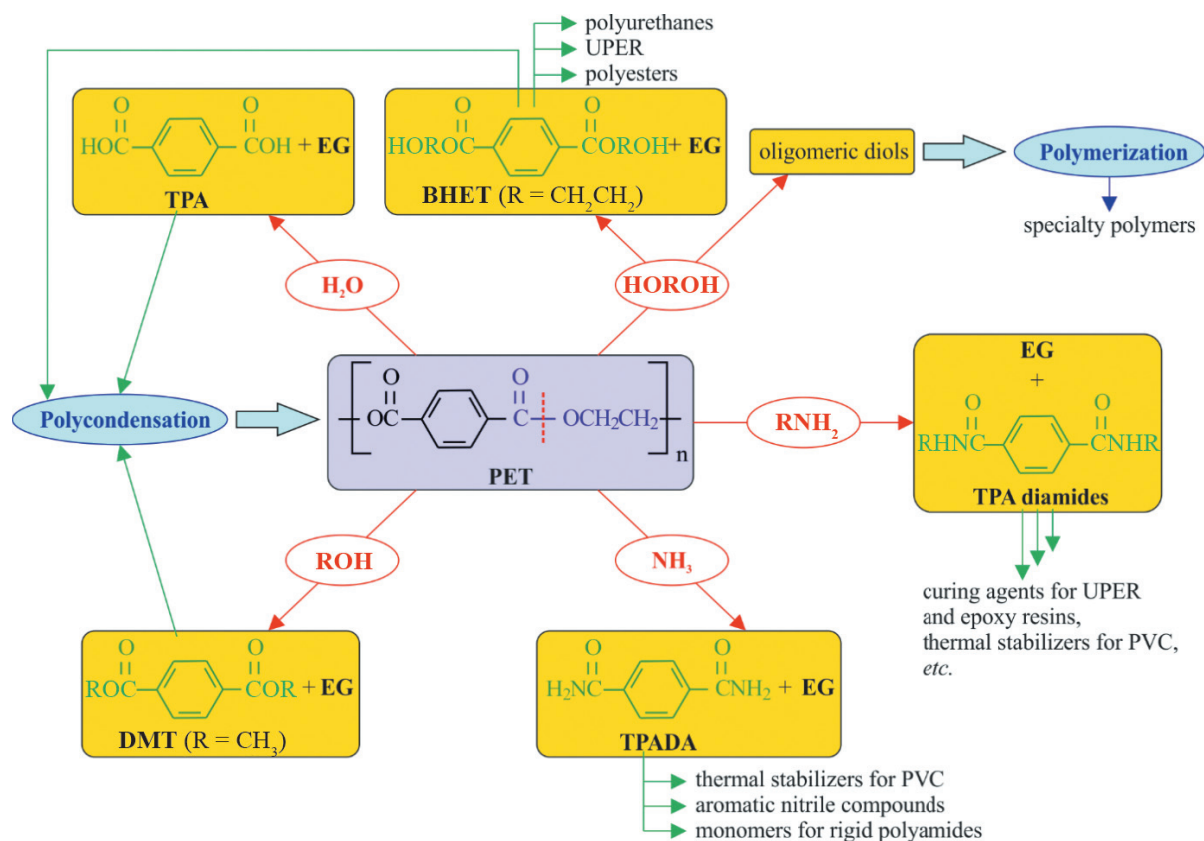


Fig. 2. General routes and main products of a destructive chemical recycling of polyesters on example of PET; abbreviations: EG – ethylene glycol, UPER – unsaturated polyester resin

phatic amines [54–62]. In most cases, those processes are directed at the complete degradation of the polymer chain and the transformation of polyester waste into monomers such as [bis(2-hydroxyethyl terephthalate) (BHET), dimethyl terephthalate (DMT), terephthalic acid (TPA) and ethylene glycol (EG)], as well as some other low molecular weight organic compounds that can be used as plasticizers. It is also possible to carry out partial chemolysis of polyesters and then utilize the resulting oligomers in the synthesis of new types of polymers (Fig. 2). Currently, of a great significance to the industry are processes of PET hydrolysis, methanolysis and glycolysis leading to the formation of terephthalic monomers (TPA, DMT, BHET) used for re-polycondensation of PET, or short-chain oligomers utilized in the synthesis of polyesters and polyurethanes [63].

PET decomposition processes will be discussed in more detail later in this study. Many of these strategies are currently being tested for PLA [64–67] and other groups of polymers containing reactive bonds in the backbone. In the case of polyesters obtained by ring-opening polymerization, *e.g.* PLA or poly(ϵ -caprolactone), it is also possible to recover monomers by pyrolysis. The depolymerization reaction involves the release of the cyclic monomer as a result of the attack of terminal hydroxyl groups on the corresponding carbon atom in carbonyl groups. These processes are not selective, and apart from the desired monomer, a number of by-products are for-

med, which are difficult to remove afterwards. However, there are some reports indicating the possibility of obtaining very pure L,L-lactide isomer as a result of the pyrolysis of commercial types of L-PLA carried out in the presence of certain compounds with weak basic properties, such as MgO or $Al(OH)_3$ [68, 69].

PET hydrolysis

Hydrolytic degradation of PET can be carried out in an alkaline, acidic and neutral environment [70].

Basic hydrolysis of PET is usually carried out for 3–5 hours at temperature of 210–250 °C and pressure of 1.4–2.0 MPa, in the presence of 4–20 wt % NaOH or KOH aqueous solutions. The products of this process are EG and TPA salt. In the next step, the solution is filtered in order to remove insoluble impurities, and then neutralized with strong acid (*e.g.* H_2SO_4) to obtain pure TPA, which is subsequently filtered off, washed with water and dried. EG remains in the reaction mixture and can be separated by extraction or distillation. The main advantages of this process include a high tolerance to the impurities in the post-consumer plastic [71]. Numerous attempts are made to reduce the temperature of this process, by using microwave radiation and selection of the proper catalysts [72, 73]. For example, the use of microwave radiation and triethylmethylammonium bromide allows to achieve almost complete hydrolysis of PET at 180 °C in about 30 minutes.

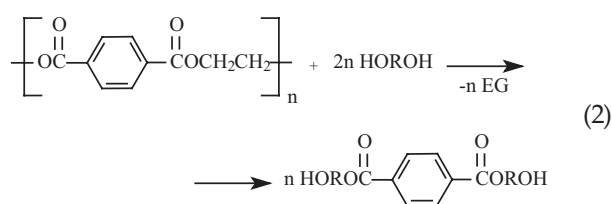
PET hydrolysis in a neutral environment usually takes place in pressure reactors at 200–300 °C and under pressure of 1–4 MPa. The weight ratio of waste PET to water ranges from 1 : 2 to 1 : 12 [70]. Products of such process are TPA and EG. The most commonly used catalysts are zinc or sodium salts [74]. The main advantages of this method include the generation of much smaller amounts of inorganic salts, which are difficult to remove later in the process. Therefore, it can be considered more environmentally friendly. However, the main disadvantage of this method is the formation of low purity TPA, since it contains all solid impurities found in PET waste [75].

In general, PET hydrolysis in an acidic environment is carried out in the presence of sulfuric, nitric or phosphoric acid. Hydrolysis in dilute (<10 M) sulfuric acid proceeds effectively at 150 °C [76, 77]. The reaction temperature and pressure can be lowered by using the concentrated (≥ 14.5 M) sulfuric acid [78]. However, this process is very expensive due to the additional operations, such as separation and purification of sulfuric acid and EG. Hydrolysis in the presence of nitric acid (7–13 M) is carried out at temperature between 70 °C and 100 °C, however, it requires long reaction time (70 hours). The advantage of this method is the direct oxidation of EG to oxalic acid [79].

PET glycolysis

Glycolysis is one of the earliest developed and the most economically advantageous methods of chemical recycling of post-consumer PET waste that can be easily implemented in industry [80]. Because of that it found its practical applications very quickly [81–86], and such powerful chemical companies as Du Pont, Goodyear, Eastman Kodak, Shell Polyester or Zimmer AG successfully started to commercialize it. Since the early 1960s, researchers in Poland have also studied this process [86–89], and nowadays, for example, it is utilized in the production of polyester resins by Ciech Sarzyna S.A. (Nowa Sarzyna, POLIMAL® terephthalic resins) [90] or LERG (Pustków, ESTROMAL® terephthalic resins) [90, 91].

During PET glycolysis, the ester bond is cleaved as a result of a nucleophilic attack of the OH groups derived from polyhydric alcohol molecules (most often diols) [Equation (2)]. Since this is a transesterification reaction its main products are EG and bis(ω -hydroxyalkyl) terephthalate (full glycolysis) or the hydroxyl-terminated PET oligomers (partial glycolysis).



Due to the relatively high boiling points of the most frequently used diols and the increased nucleophilicity of their hydroxyl groups with respect to water, glycolysis of polyesters is carried out at atmospheric pressure and the reagents are heated up to 300 °C (usually the temperature is maintained between 170 °C and 270 °C) [56]. The process parameters exceeding those limits are used very rarely, although there are some reports in the literature regarding a high-pressure glycolysis [92, 93], as well as glycolysis conducted under sub- or supercritical conditions (temperatures of 300–450 °C and pressure within 1.1–15.3 MPa) [94]. For ecological reasons, it is also rarely proposed to conduct glycolysis in the presence of an additional solvent, *e.g.* xylene, which increases the efficiency of the process by ensuring a better miscibility of the reagents and shifting its equilibrium in favor of depolymerization due to dissolution of PET degradation products [95]. One of the innovations improving the economics of PET glycolytic degradation is the replacement of a classic convection or electric heating with microwave heating, which allows to minimize the time required to achieve an identical degree of polymer waste's conversion by several times – this is due to a very good absorption of microwave radiation by glycols [96–98]. It has been also found that the glycolysis of ester bonds is favored, if the polymer raw material is irradiated with electrons (an electron beam pre-treatment) [99].

In order to fully degrade PET all hydroxyl reagents are used in several-fold molar excess with respect to monomeric units of the polymer. These substrates can be divided into the following groups:

- ethylene glycol and its oligomers [56, 93–103], as well as propylene glycol [92, 101] and its oligomers [104]. EG is the most commonly applied glycolytic agent due to the possibility of a direct processing of PET waste into its monomer (BHET), which can replace a part or all of the raw material obtained from petroleum [56]. Since the increase in molecular weight lowers diol reactivity in glycolysis processes, the replacement of EG by its oligomers results in a partial depolymerization of PET and the formation of polyols [98];
- linear and branched alkanediols, *e.g.* C4–C10 linear diols [105], neopentyl glycol [104, 106];
- polyhydric alcohols, *e.g.* glycerol [98, 107] or 1,1,1-trimethylolpropane [108]. This group also includes tertiary alkanolamines [63, 109].

An interesting group of PET degrading agents may constitute triglycerides containing hydroxyl groups, which can be found in different vegetable oils, *e.g.* castor oil. Since these substrates come from renewable sources it is predicted that their use could make PET glycolysis more environmentally friendly [110].

Catalysts used in the PET glycolysis process

The glycolytic degradation of polyester does not require the use of catalysts, however, the process takes place relatively slowly [57, 61]. Several studies have shown that the

presence and concentration of a catalyst have the greatest impact on the kinetics of polyester glycolysis, followed by some other operational variables such as temperature and time [55]. Due to its nature, this process can be catalysed by many classic systems used in transesterification, and thus also in PET synthesis {e.g. $\text{Ti}(\text{OBu})_4$ [111]}. Currently, the most popular are heavy metal salts (Zn, Mn, Co, Pb, Cu, Fe, Ti, Pr/Nd) with acetate, diorganophosphate or sulfate anions [56, 57], as well as chlorides [112]. However, acetic acid derivatives (their activities regarding the ester bond cleavage lowering in the following order: $\text{Zn} > \text{Mn} > \text{Co} > \text{Pb}$) seem to give way to derivatives of phosphoric acid diesters that are more active and selective toward monomeric bis(ω -hydroxyalkyl) terephthalate [113]. In recent years, some efforts have been made to replace these toxic systems with more environmentally friendly catalysts such as weak bases (Na_2CO_3 , NaHCO_3) and less reactive sodium or potassium sulfates [114, 115], as well as a mixture of calcium oxide and hydroxide obtained during calcination of animal shells derived from oysters or chicken eggs [116]. For that purpose alkali or alkaline earth metal hydroxides {e.g. NaOH [97], $\text{Ba}(\text{OH})_2$ [96]} can be also applied.

Apart from their toxicity, the disadvantages of the above mentioned ester bond glycolysis catalysts also include problems with their regeneration/separation from the post-reaction mixture – all these catalytic systems usually exhibit good solubility in glycols used in the process [57]. In order to minimize this problem, a number of new catalysts have been proposed. They are based on non-volatile, non-toxic and thermally stable ionic liquids, both neutral as well as exhibiting the properties of protic and Lewis acids or bases – a comprehensive review of such catalytic systems is included in the work of Jehanno *et al.* [117], George and Kurian [118] and Al-Sabagh and co-workers [57]. Some alternative to using expensive ionic liquids are so-called deep eutectic solvents, e.g. those based on urea, for which biodegradability can be an advantage, in addition to economic considerations [119]. In the process of glycolysis of esters, enzymatic catalysis is also reported in the literature, for example Machado de Castro and Carniel have shown that the application of this type of catalysis does not have to be limited only to hydrolytic degradation and allows PET degradation in very mild conditions [120].

A separate category of catalysts that can be quite easily regenerated and used repeatedly in glycolysis of polyesters are some heterogeneous systems including: polyoxometalates [121], sodium metasilicate [122], metal oxides (e.g. derivatives of Zn, Mn, Fe, Ca, Ba, Sr) used directly or supported on nano- and microsilica particles [57, 118], double metal hydroxides with a layered structure [123, 124], as well as hydrotalcite, solid superacids ($\text{SO}_4^{2-}/\text{ZnO}$ and $\text{SO}_4^{2-}/\text{TiO}_2$) and zeolites [57, 118].

Areas of application for PET glycolysis products

The products of a partial or full PET glycolysis are used primarily as raw materials in the synthesis of new groups

of unsaturated polyester resins, alkyd resins, polyurethanes, epoxy resins and vinyl (oligo)esters [62, 118, 125]. In the case of BHET, re-polymerization processes are still of great importance, because the product of PET waste glycolysis can partially replace or completely eliminate the raw material of a petrochemical origin [126].

UPER can be synthesized by polycondensation of equimolar amounts of PET glycolysate with unsaturated dicarboxylic acids or their anhydrides (e.g. maleic anhydride). In order to reduce the concentration of unsaturated bonds in the resulting polyester a saturated dicarboxylic acid, usually adipic acid, is also added to the reaction mixture [118]. UPER containing terminal unsaturated groups can also be obtained by condensation of PET glycolysate with unsaturated monocarboxylic acids, e.g. oleic acid [127]. The properties of the polyester composition obtained in this manner, both before and after cross-linking, largely depend on the type of diol used for degradation of PET. For the purpose of UPER synthesis, the most commonly used are PET glycolysates derived either from EG or its short oligomers (the latter giving adequate flexibility to the final polyester), as well as propylene glycol responsible for an improvement of polyester miscibility with the crosslinking monomer [118]. However, glycolysates derived from those low molecular weight diols can be replaced with oligoester diols that are produced in the course of a partial PET glycolysis [62, 86, 118]. UPER containing PET glycolysates can be applied as polymer matrix in composites with inorganic fillers, which after hardening form the so-called polymer concretes [118].

Alkyd resins obtained as a result of condensation of polyhydric alcohols with polycarboxylic acids constitute an important group of coating materials. PET glycolysates derived from diols, glycerine, pentaerythritol and/or vegetable oils can also be utilized in their synthesis leading to the formation of air-drying materials exhibiting excellent mechanical properties, good chemical resistance and good adhesion to the metal surface, as well as containing very low concentrations of volatile organic compounds (VOCs) harmful to the environment [118, 128–130]. It is worth noting that they can also form very pro-ecological water-borne systems [129].

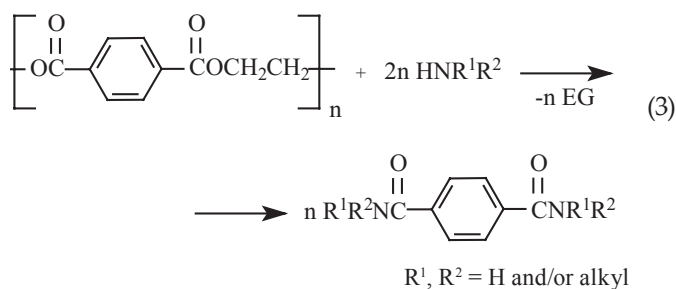
In the area of polyurethanes, oligomeric or monomeric (e.g. BHET [131]) hydroxyl-terminated PET glycolysates are thought to be very interesting substitutes for classic polyol components that react with diisocyanates. They can be used directly [63, 98, 109, 131], or first polycondensed with some aliphatic dicarboxylic acid or its anhydride [108], as well as triglyceride [100–102]. A variation of the latter method is the esterification of PET glycolysate with unsaturated monocarboxylic acid, combined with epoxidation of unsaturated bonds and their subsequent hydrolysis [99]. The obtained polyurethanes, depending on their structure (e.g. chemical structure of PET glycolysate), can be effectively used in preparation of polyurethane foams [63, 98, 109, 131], polyurethane adhesives and coatings [99–102, 108, 118].

Polyesters formed during PET glycolysis can be applied as components of epoxy adhesive and film-forming compositions, in which they can function either as hardeners (*e.g.* PET degraded with trialkanolamine [63]), or base resins subjected to cross-linking by the addition of some auxiliary hardener, *e.g.* melamine–formaldehyde resin [132].

PET glycolysate containing terminal epoxy groups derived from epichlorohydrin [132, 133] constitutes a valuable raw material in the synthesis of UV-curable vinyl resins: the unsaturated moiety is introduced into them as a result of the addition of acrylic or methacrylic acid [133]. A similar bifunctional diacrylate or diallyl oligomer can be obtained by the esterification of glycolysate terminal hydroxyl groups with acryloyl chloride or allyl chloroformate, respectively [134].

Ammonolysis and aminolysis of PET

PET degradation processes induced by ammonia (ammonolysis) or primary and secondary amines (aminolysis) are an interesting alternative to conventional methods of PET raw material recycling (hydrolysis or alcoholysis/glycolysis reactions) because they can be conducted under milder temperature and pressure conditions. Due to their increased basicity, both amines and NH_3 cleave ester bonds much easier and faster compared to the OH groups present in water or alcohol molecules [56, 135, 136]. Such reaction results in the transformation of PET waste into low-molecular TPA amides according to Equation (3).



Of the nitrogenous compounds, ammonia is relatively rarely proposed as a degrading agent for PET macromolecules, which can be explained by its lower reactivity compared to amines and the limited possibilities of economically justified utilization of the produced terephthalic acid diamide (TPADA) [54]. Literature data show that TPADA can be used as an additive increasing the thermal resistance of PVC [137, 138] or transformed, in the process of pyrolytic dehydration, into a number of other aromatic nitrile compounds (1,4-dicyanobenzene, 4-cyanobenzoic acid and its amide) [139, 140]. It is worth emphasizing that aromatic nitriles can be further hydrogenated to the appropriate reactive aminomethyl derivatives [*p*-xylene diamine, 4-(aminomethyl)benzoic acid], which are attractive monomers in the synthesis of polyamides – they can improve the economy of the entire process of PET ammonolysis [60, 141].

It was shown that ammonolytic degradation of PET can be carried out with high efficiency in the presence of EG [139–141] and water [137, 142–144]. Table 1 summarizes the literature data on PET ammonolysis.

Usually this process does not require heating or pressure reactors, and ammonia is used in the form of an aqueous solution [137, 138, 142–144]. However, a fairly long time is required to achieve a complete conversion of PET waste (up to 45 days). In order to shorten the whole process to a few hours, an elevated temperature (>100 °C) and a proper catalyst (cetyl bromide [142] or zinc acetate [143]) can be used.

Compared to ammonolysis, the degradation of PET under the influence of amines is much more popular, due to a higher reactivity of the amino group in the ester bond cleavage, as well as the possibility of a simple synthesis of *N*-substituted or *N,N*-disubstituted derivatives of TPA diamides having different organic groups [145, 146]. Among the tested systems were both simple derivatives with monofunctional alkyl groups (*e.g.* Me [137, 142, 144, 147, 148], Et [147], ⁿBu [137, 147, 148]) or phenyl substituents [146], as well as more complex compo-

Table 1. Reaction conditions and yields of PET ammonolysis

| Temperature °C | Pressure MPa | Time ^a | Reaction medium | Catalyst | TPADA yield % | Ref. ^b |
|-----------------|------------------|-------------------|------------------------------|------------------------------|-----------------|-------------------|
| 25 ^c | 0.1 ^c | 60 d | 40% $\text{NH}_3(\text{aq})$ | – | nd ^d | [137] |
| 25 ^c | 0.1 ^c | nd | 40% $\text{NH}_3(\text{aq})$ | – | nd | [138] |
| 120–180 | <i>ca.</i> 0.86 | 1–7 h | EG/ $\text{NH}_3(\text{l})$ | – | 50–93 | [139, 140] |
| 100–140 | 0.1–1.0 | 1.5–20 h | EG/ $\text{NH}_3(\text{g})$ | – | >95 | [141] |
| 40 | 0.1 ^c | 3–45 d | $\text{NH}_3(\text{aq})$ | – | 8–45 | [142, 144] |
| 40 | 0.1 ^c | 3–45 d | $\text{NH}_3(\text{aq})$ | Cet NH_3Br^a | 7–37 | [142] |
| 25 ^c | 0.1 ^c | 3–45 d | $\text{NH}_3(\text{aq})$ | $\text{Zn}(\text{OAc})_2^a$ | nd | [143] |

^a Abbreviations: nd – not determined/not described, h – hour, d – day, Cet – *n*-hexadecyl group, $\text{Zn}(\text{OAc})_2$ – zinc acetate dihydrate.

^b References.

^c Processes carried out in ambient conditions - no specific conditions were given in the experimental section, thus, atmospheric pressure and temperature of 25 °C were assumed.

^d 100% of PET conversion.

unds active in click-chemistry reactions [145, 146]. Due to their potential applications, two groups of reactive, *N*-substituted terephthalamides containing the OH or amino groups are of particular interest to researchers. The first of them are the products of the reaction between PET and alkanolamines, for example ethanolamine [136, 145, 146, 148–155], 3-amino-1-propanol [155, 156], 2-amino-2-methyl-1-propanol [157], 1-amino-2-propanol [157] and diethanolamine [158]. On the other hand the amino functionality can be introduced by using bi-functional degradation agents like hydrazine [159, 160] and its homologues with the C2–C6 alkane chains [145, 146, 161], aliphatic diamines containing aromatic rings (*e.g.* benzylamine and its derivatives, xylene diamine isomers [145, 146]), aromatic diamines (*e.g.* phenylenediamine isomers [146]), as well as heterocyclic diamines (piperidine, piperazine and pyridine derivatives [145, 146]). Aliphatic polyamines of the general formula $H_2NCH_2CH_2(NHCH_2CH_2)_xNH_2$ where $x \leq 3$ [135, 162] can be also used for the same purpose.

Aminolytic degradation of PET does not require the use of extreme process conditions and advanced apparatus or anhydrous environment. However, depending on the amine used, a simple mixing of substrates at atmospheric pressure and ambient temperature (25–40 °C) results in a complete conversion of waste PET only after a several days [137, 142, 144, 147, 148]. This time can be reduced to few hours by increasing temperature and using suitable catalysts, which increase the electrophilicity of carbonyl carbon in an ester bond [151]. The reported systems include metal salts (sodium acetate, zinc acetate, K_2SO_4 , Na_2SO_4 , $MgCl_2/NiCl_2$) [136, 151, 157, 159, 160], carboxylic acids (*e.g.* acetic acid) [151], quaternary ammonium salts (*e.g.* cetyltrimethylammonium bromide) [153] as well as organotin compounds (dibutyltin oxide) [152, 153] and bicyclic nitrogen bases (*e.g.* 1,5,7-triazabicyclo[4.4.0]dec-5-en) [145, 146]. It is also very beneficial to run the entire process in a microwave reactor, which allows the conversion of waste PET to the desired product within several minutes [154, 159, 160]. Utilization of an organic solvent having a high boiling point, *e.g.* xylene, is rarely proposed, since the whole process has to be carried out in an autoclave [163].

The products of PET deep aminolysis have not been applied in the chemical industry on the large scale. Based on the analysis of the results of research work described in the scientific literature, the following directions for the use of *N*-substituted terephthalamides can be identified:

- epoxy resins cross-linking agents, for example PET aminolysates obtained as a result of the action of ethylenediamine [145, 161] and its homologues (polyamines) [135, 145], as well as xylene diamine [145];
- cross-linking agents for UPER, *e.g.* a derivative containing allyl moieties [164];
- PVC plasticizers (*e.g.* hydrazine derivative [165] or products of the reaction between ω -hydroxyphthalamides and C7–C10 alkane acids [136, 155]);

- thermal stabilizing additives for PVC [137] and LDPE [166];
- substrates in the synthesis of UV-curable acrylic adhesion promoters for the metal-glass systems [167];
- substrates in the synthesis of polyesters [168] and polyurethanes (*e.g.* rigid foams [135], adhesive materials [150] and biodegradable systems [149]). Usually, for that purpose ω -hydroxyphthalamides obtained from ethanolamine and diethanolamine are used;
- components of the film-forming alkyd resins cross-linking in air or thermally [163];
- components of mixtures used for preparation of anti-corrosion paints [153], as well as additives for bituminous mixtures and asphalt [162, 169, 170];
- substrates in the synthesis of antibacterial and antifungal agents, especially the derivatives of hydrazine and ethylenediamine [160, 171].

It should be noted that incomplete (surface) aminolysis processes are already used by industry to modify the properties of PET fibers [172–174].

SUMMARY

Although this study does not exhaust all the existing possibilities of chemical recycling of polyesters, it is clear that a very solid basis has been made for its use in the recycling of many types of polycondensation materials or their analogues obtained by other polymerization methods. The key limitations are both a selective collection of plastic wastes and their initial cleaning. So far, this solution is implemented almost exclusively for products made of PET and certain polyurethane species (obtained by polyaddition). This is mainly due to the large scale of production of these materials. There is no doubt that both the marketing and legislative issues will promote the extension of chemical recycling methods to other groups of polymer materials. At the presents stage, the simplest solution seems to be the dissemination of the constructive recycling method based on the chain extenders because it does not require large capital expenditure and can be used for the post-production waste treatment in plastic processing plants.

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opracował ogólnokrajową

BAZĘ APARATURY DO OKREŚLANIA CHARAKTERYSTYKI I PRZETWÓRSTWA POLIMERÓW

będącej w posiadaniu uczelni, instytutów PAN i instytutów badawczych.

Baza jest wyposażona w funkcje umożliwiające wyszukiwanie wg zadanych parametrów: nazwy, typu lub modelu aparatu, roku produkcji, producenta, charakterystyki parametrów technicznych, zastosowania do badań, lokalizacji, słów kluczowych, sposobu wykonywania badań, numerów norm, wg których prowadzi się badania, oraz adresu i kontaktu z osobą odpowiedzialną za dany aparat.

Baza jest ciągle uaktualniana.

Dostęp do danych i wyszukiwanie informacji w bazie jest bezpłatne.

Instytucje i firmy zainteresowane zamieszczeniem w bazie informacji o posiadanej aparaturze prosimy o przesłanie danych na adres polimery@ichp.pl

aparaturapolimery.ichp.pl